ABSORPTION SPECTRA OF ORGANIC SUBSTANCES IN THE LIQUID AND SOLID STATES—II. CRESOLS*

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Plate IV

ABSTRACT. The absorption spectra of extremely thin films of *o*-, *m*-, and *p*-cresols in the liquid state and in the solid state at low temperatures have been investigated, and bands have been observed. The results have been compared with those reported by previous workers for the vapour state of the substances and also for the solution of these substances in heptane. It has been observed that in all the three cases, the number of bands diminish with the liquefaction of the substance and further the ν_0-band shifts towards the longer wavelength. It is pointed out that such a shift may be due to association of molecules in the liquid state and the diminution in the number of bands with liquefaction may be due to the influence of the impact of the surrounding molecules on the vibration of individual molecules in the liquid. It is further observed that the bands shift towards shorter wavelength when the liquids are solidified and in the case of *p*-cresol, the number of bands increases with solidification. The companions of the ν_0-band in the case of *p*-cresol represent transitions to higher harmonics of the mode of frequency 825 cm^{-1} of the benzene nucleus. It is pointed out that the increase in the electronic energy of the molecule with solidification may be due to contraction of the molecules which also increases the frequency of some of the modes of vibration of the molecule. Also, it is concluded that higher harmonics of some of the modes of vibration are allowed in the case of solid *p*-cresol probably because the pseudo-symmetry of the molecule in the crystal allows some space around the benzene nucleus of the molecule.

INTRODUCTION

The ultraviolet absorption spectra of aromatic molecules in the vapour state have a number of characteristic features. Most aromatic compounds absorb light in the region 2500 – 3000 A owing to an electronic transition involving the excitation of the pi–electrons in the ring corresponding to the $A_{1g} - B_{2u}$ transition in benzene, the direct excitation from the ground state to higher state being forbidden. The ultraviolet absorption of aromatics in the liquid state has been widely used in analysis. The fine structure of the spectrum is largely wiped out in the liquid state, the bands being in general broad. Kronenberger (1926) has found that in the case of benzene, the broad bands in the liquid state become sharper at liquid oxygen tem-

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perature. Recently, Broude *et al* (1950) have reported the results of investigations on the ultraviolet absorption spectra of a large number of substituted benzene compounds at low temperatures upto that of liquid hydrogen in some cases. The journal in which the results were published is in Russian and being not available to the author it could not be ascertained whether the authors mentioned above have studied the absorption spectra of cresols and whether they have actually compared the absorption spectra of the substances in the liquid state with those for the solid state in order to find out whether any significant changes occur with solidification of the substances. The present work is part of a programme aimed at studying the influence of change of state and lowering of temperature on the absorption spectra of organic substances and especially of substituted benzene compounds, and correlating the results with those observed in the investigations on the Raman spectra of those substances in different states. In the present investigation, the ultraviolet absorption spectra of *o*-, *m*-, and *p*-cresols have been investigated in the liquid and solid states at different temperatures.

EXPERIMENTAL

The experimental set up is that employed in an earlier investigation by the author (Swamy, 1951). The source of continuous spectrum used was a hydrogen discharge tube. Spectrograms were taken on Ilford HP3 films on a Hilger E_1 spectrograph having a dispersion of 3 A. U. per mm. in the region 2600 A°. Chemically pure BDH cresols distilled four times in vacuum were used in this investigation.

Previous workers (Purvis and McCleland, 1913), who investigated the absorption spectra of cresols in the liquid state, were not able to get bands probably because their films were too thick and produced continuous absorption over a wide range of wavelengths. It was found in the present investigation that a film of a thickness of a few microns produced the bands. Such a film was produced when a very small drop of the liquid was placed between two quartz plates and one of the quartz plates was slided till colours were produced by the thin film.

The study of the absorption spectra at low temperatures was carried out using the arrangement described by the author in a previous paper (Swamy, 1951). Copper plates were attached to the brass frame containing the cell and the plates were made to dip in liquid oxygen, while the brass frame was kept much above the level of liquid oxygen in order to keep the sample at $-150°C$. To maintain the sample at $-180°C$, the level of liquid oxygen was so adjusted that the lower part of the brass frame came in contact with the liquid oxygen. An exposure of 45 minutes was necessary to record the absorption spectrum for the solid state, while with proper alignment an exposure of 10 minutes was required to record the absorption spectra for the liquid state. For comparison, mercury arc spectrum was recorded with the help of Hartmann diaphragm on each spectrogram.

RESULTS

Three sets of spectrograms for *o*-, *m*-, and *p*-cresol in the liquid and solid states are reproduced in Plate IV. The wave numbers of the bands observed are given in Tables I, II and III in which wave numbers of the bands observed in the vapour state and also in solution by previous workers are included for comparison.

TABLE I

Absorption bands of *o*-cresol. ν in cm^{-1}

Band No.	Purvis & McCleland (1913)	Robertson, Ginsberg and Matsen (1936) Prominent bands		Wolf and Herold (1931)		Present author		
	Vapour			Solution in heptane		Liquid at 30°C	Solid at −180°C	Assignment
1	35387(w)							
2	Bet 36025 & 36260(w)	36247	ν_0	35950(S)	ν_0	35982 (Broad)	36109	ν_0
3	37094(w)	36432	ν_0+185	36881(m)	ν_0+931	36789 (Broad)	36978	ν_0+869
4	37219 (fst)	37108	ν_0+861	37450(vw)	ν_0+1500			
5	37400			38450(vw)	ν_0+931 $+1500$			

TABLE II

Absorption bands of *m*-cresol. ν in cm^{-1}

Band No.	Purvis and McCleland (1913)	Wolf and Herold (1931)		Present author			
	Vapour	Solution in heptane		Liquid at 30°C	Solid at −150°C	Solid at −180°C	Assignment
		35761(S)	ν_0	35806(S) Broad	35831	38851	ν_0
1	35986 f str						
2	36077 ,,			875			
3	36142 ,,						
4	36300 ,,						
5	Bet 36592 & 37149 vw diff	36740(m)	ν_0+979	36681(S) (Broad)	36713	36774	ν_0+893
6	37246 w	37302(vw)	ν_0+1541				
7	37810 ,.						
8	37896 ,,						
9	37968 ,,						
10	38011 ,,						
11	38112 ,,						
12	38185 ,,						

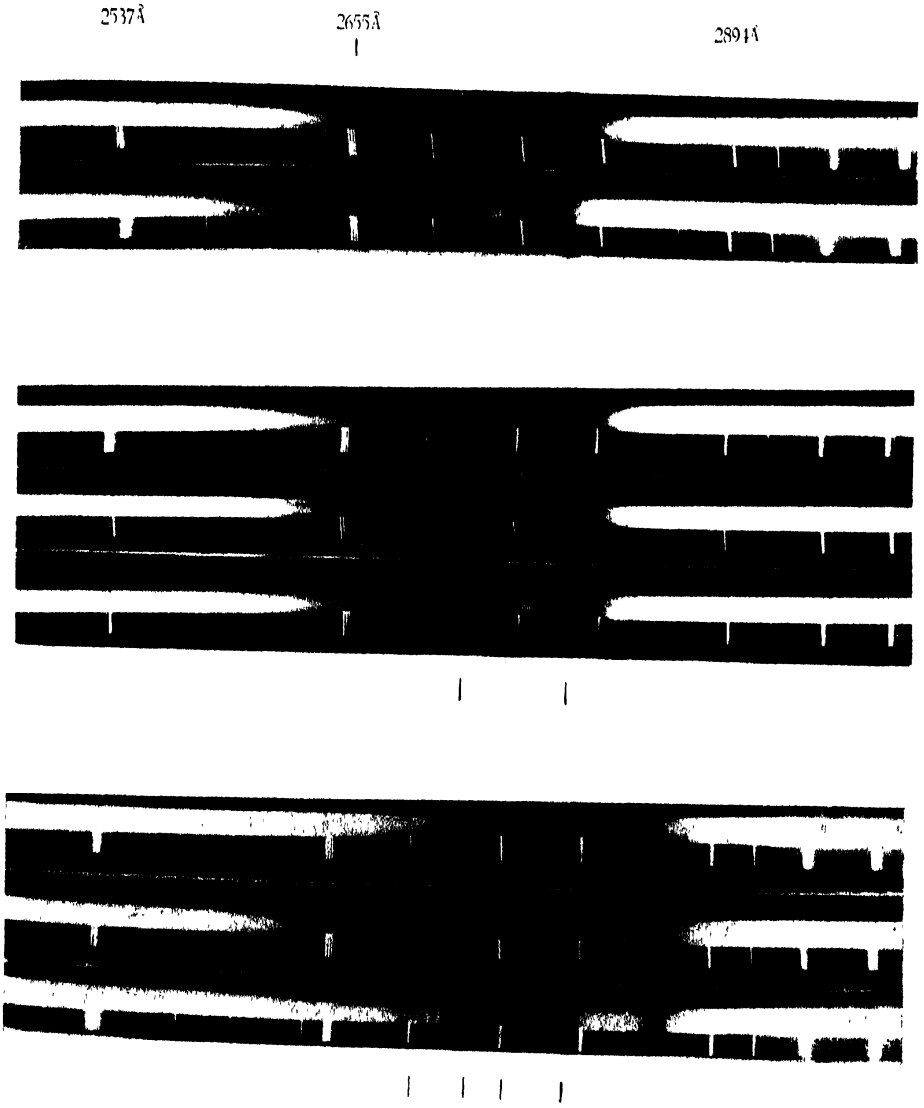
TABLE III

Absorption bands of *p*-cresol. ν in cm^{-1}

Band No.	Robertson, Ginsberg and Matsen (1946). Prominent bands		Wolf and Herold (1931)	Present author			
	Vapour	Assignment	Solution in heptane	Liquid at 30°C	Solid at −150°C	Solid at −180°C	Assignment
1	35325(vs)	ν_0	34960(s) 35430(w)	35044 (Broad)	35011(s)	35020(vs)	ν_0
2	36116(s)	ν_0+791	35810(s)				
3	36512(s)	ν_0+1187	36220(s)	35957 (Broad)	35857(s) 36260(s)	35845(s) 36234(s)	ν_0+825 ν_0+1211
4	36916(s)	$\nu_0+2\times791$	36970(s)		37067(m)	36673(s)	$\nu_0+2\times825$
5	37302(m)	$\nu_0+1187+791$	37440(m)			37056(m)	$\nu_0+825+1211$
6	37724(w)	$\nu_0+3\times791$	37720(m) 38120(w)				
7	38127(w)	$\nu_0+2\times791+1187$					

DISCUSSION

The results given in Tables I, II, III show that there are some general features in the changes which take place in the absorption spectra with the change of state. First, the number of bands in the vapour state is much larger than that observed either in the liquid state or in the solid state. Secondly in all these three cases the principal absorption band due to transition from the ground state as well as its companions shift towards the longer wavelength side with the liquefaction of the vapour, and when the liquid is solidified these bands shift towards the shorter wavelength side. In the vapour state most of the bands are due to transitions of the electron to the higher energy state accompanied by transitions to vibrational energy states of different quantum numbers up to a large value of the latter. The diminution in the number of the bands in the liquid state may be due to the influence of translational motion of the molecules in the liquid in the state of aggregation. Probably, constant impact of the neighbouring molecules hinders transitions to higher vibrational energy states. In the solid state the molecules are a little closer together and there is little room for much expansion of the molecule during different modes of oscillation. Hence such modes may be quenched in the solid state. There may be exceptions, however, in which case the regularity of the arrangement of the molecules together with peculiar



Absorption spectra of cresols.

Fig. 1. *o*-cresol
(*a*) Liquid at 30 C
(*b*) Solid at –180 C

Fig. 2. *m*-cresol
(*a*) Liquid at 30 C
(*b*) Solid at—150 C
(*c*) Solid at –180 C

Fig. 3 *p*-cresol
(*a*) Liquid at 30 C
(*b*) Solid at 150 C
(*c*) Solid at—180 C

structure of the molecule may be responsible for peculiar type of packing in the solid state, in which the benzene ring may have some surrounding empty space to execute some modes of oscillation of higher quantum numbers. We shall now discuss the results for the three substances separately.

(*a*) *o-Cresol.* The results obtained by Robertson, Ginsberg, Matsen (1946) for the vapour state of *o*-cresol have been included in Table I. Tentative assignment has been made in column 4 of the frequencies observed. It is found that the vibrational frequencies 185 and 861 cm^{-1} are represented in the bands. Probably the latter frequency represents the breathing vibration of the benzene nucleus in the excited state in the case of the vapour. On making an attempt to assign the frequencies observed in the case of solution of ortho-cresol in heptane by Wolf and Herold (1931) it is found that the frequencies deduced from these bands are 931 and 1500 cm^{-1}, which are quite different from those observed in the case of the vapour. In the present investigation for the liquid and solid states much fewer bands are observed. The ν_0-band seems to have shifted from 36247 to 35982 cm^{-1} on liquefaction and only a companion representing the transition $\nu_0 + 807$ cm^{-1} is present. Thus the bands shift towards longer wavelength. This may be due to the fact that in the liquid state molecules become associated with one another through virtual bonds and the electronic energy state is lowered during this process. The solid at $-180°C$ also exhibits two bands. The ν_0-band eventually shifts again to shorter wavelength side and the companion represents the frequency $\nu_0 + 869$ cm^{-1}. This increase in the value of the difference of energy between the two states is probably due to the contraction of the molecule itself in the solid at low temperature The vibrational freqency of the ring also seems to increase a little in the solid state.

(*b*) *m-Cresol.* In this case the data reported by Purvis and McCleland (1913) showed that there are numerous bands besides the ν_0-band. These companions of the ν_0-band are due to the vibrational transitions as in the case of *o*-cresol. The data for solution in heptane reported by Wolf and Herold (1931) show vibrational frequencies 979, and 1541 cm^{-1}. These frequencies can be reconciled only with those for the ground state of the molecule observed in the Raman spectra and not with those for the excited state. The frequencies observed in the Raman spectra for *o*-, *m*-, and *p*-cresol are quite different from each other. This shows that the relative positions of the substitution groups have much influence on the vibrational frequency of the benzene ring. In the case of *m*-cresol in the liquid state only two bands are observed in the present investigation. Both these are displaced towards longer wavelengths from the position of the corresponding bands in the vapour state. This again shows that there may be formation of virtual bonds among neighbouring molecules in this case also, as explained above. The second band represents the transition $\nu_0 + 875$ cm^{-1} which shows that the vibrational frequencies of the excited state of the molecule in the liquid is 875 cm^{-1}. In the solid state at $-150°C$, both these bands shift towards shorter wave-

length by about 25 cm^{-1}, but when further cooled down to $-180°C$, the the solid gives two bands shifted still further towards shorter wavelength and the vibrational frequency increases to 893 cm^{-1}. This again may be due to contraction of the molecule in the solid state.

(*c*) *p Cresol.* The results for *p*-cresol observed in the present investigation show some characteristics difference from those observed in the case of the other two cresols. The data for the vapour reported by Robertson, Ginsberg and Matsen (1946) are given in column (2) of Table III. Taking ν_0 to be 35325 cm^{-1}, the assignment of other bands leads to vibrational frequencies 791 and 1187 cm^{-1} are as shown in column 3 of the table. It is also found that transitions up to a value of the quantum number equal to 3 occurs in this case for the mode of frequency 791 cm^{-1}, The data for the solution reported by Wolf and Herold (1931) cannot be classified satisfactorily according to such a scheme. Probably the intermolecular field of the solvent has influence on the electronic energy states of molecule. In the liquid state *p*-cresol yields only two bands, the second band representing the transition $\nu_0 + 913$ cm^{-1}: The soild at $-150°C$ yields 4 bands and this number increases to 5 when the solid is further cooled down to $-180°C$. It is interesting to note that the vibrational frequencies deduced from these bands are 825 and 1214 cm^{-1} in the solid state and that the transition $\nu_0 + 2x825$ cm^{-1} as well as $\nu_0 + 825 + 1214$ cm^{-1} take place in this case at the low temperature. On comparing these results with those for the vapour, it is found that on liquefaction the principal band shifts towards longer wavelength by about 300 cm^{-1} and on solidification the position remains almost the same as that in the liquid. Further, the vibrational frequency is about 791 cm^{-1} for one of the modes and 1187 cm^{-1} for the other mode in the case of the vapour, while these increase to 825 and 1214 cm^{-1} respectively in the solid state.

When the two substitution groups are in the para position, there is some symmetry in the molecule and the permanent electric moment is much smaller than that of the molecule with the substitution groups either in ortho or meta position. The influence of intermolecular field is almost identical in the liquid and solid states of *p*-cresol, probably because the value of the permanent electric moment is small. The shift of the principal band towards longer wavelength side with the liquefaction of the vapour, however, shows that in the liquid state there may be formation of virtual bonds as in the other two cases. The pseudo-symmetry of the molecule may lead to such an arrangement of the molecules in the crystal as would leave some intervening space between the benzene rings, and therefore, vibrational transitions to higher quantum energy states may be possible in this case.

It is well known that according to Davydov's theory there may be splitting of the energy levels of the molecule in the crystal due to intermolecular forces. None of the three substances mentioned above shows such splitting and in the case of *p*-cresol the extra bands can be accounted for by assuming them to be due to excitation of harmonics of certain modes of

vibration of the benzene ring. This absence of Davydov's splitting in these three cases may be due to the fact that already in the liquid state the molecules get associated with each other and the association of molecules exhibits itself in the shifting of the bands towards longer wavelength side.

Investigations with other benzene compounds are in progress and the results will be reported later.

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